

# Hole superconductivity in the electron-doped superconductor $\text{Pr}_{2-x}\text{Ce}_x\text{CuO}_4$

Y. Dagan\*

*School of Physics and Astronomy, Raymond and Beverly Sackler  
Faculty of Exact Sciences, Tel-Aviv University, Tel Aviv, 69978, Israel*

R.L. Greene

*Center for Superconductivity Research Physics Department University of Maryland College Park, MD, 20743  
(Dated: February 1, 2008)*

We measure the resistivity and Hall angle of the electron-doped superconductor  $\text{Pr}_{2-x}\text{Ce}_x\text{CuO}_4$  as a function of doping and temperature. The resistivity  $\rho_{xx}$  at temperatures  $100\text{K} < T < 300\text{K}$  is mostly sensitive to the electrons. Its temperature behavior is doping *independent* over a wide doping range and even for non superconducting samples. On the other hand, the transverse resistivity  $\rho_{xy}$ , or the Hall angle  $\theta_H$  where  $\cot(\theta_H) = \rho_{xx}/\rho_{xy}$ , is sensitive to both holes and electrons. Its temperature dependence is strongly influenced by doping, and  $\cot(\theta_H)$  can be used to identify optimum doping (the maximum  $T_c$ ) even well above the critical temperature. These results lead to a conclusion that in electron doped cuprates holes are responsible for the superconductivity.

PACS numbers: 74.25.Fy, 74.72.-h

## I. INTRODUCTION

A striking property of the high  $T_c$  cuprate superconductors is the extreme sensitivity of many of their electronic properties to the number of charge carriers put into the copper-oxygen planes (doping). From a chemical point of view these charge carriers can be either holes, as in  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ , or electrons as in  $\text{Pr}_{2-x}\text{Ce}_x\text{CuO}_4$ . However, in the electron-doped superconducting cuprates, transport<sup>1,2</sup> and angle resolved photoemission spectroscopy (ARPES) studies<sup>3</sup> have shown that both electrons and holes play a role in the normal state properties. An interesting and important question is whether both also play a role in the superconducting state<sup>4</sup>.

Conventional superconductors are characterized by a single temperature scale,  $T_c$ , above which all the information about their superconducting properties is lost and they become normal metals. This is not the case for the hole-doped cuprate superconductors. It is believed that due to strong electron correlations doping effects on many electronic properties are seen at relatively high temperatures. For example, by looking at resistivity curves of various doping levels of one compound well above  $T_c$  one can identify the location of the doping level with maximum  $T_c$  (optimum doping)<sup>5</sup>. A different picture is seen on the electron-doped side of the phase diagram. Near optimum doping the temperature dependence of the Hall coefficient ( $R_H$ ), along with some other transport properties, were interpreted as evidence for two types of carriers<sup>1,2</sup>. ARPES measurements indeed revealed an evolving Fermi surface from small electron pockets at low dopings to a Fermi surface with holes and electrons like regions with hot spots at optimum doping<sup>3,6</sup>.

In hole doped cuprates the resistivity is linear in temperature over a wide temperature range for underdoped samples extrapolating to zero at  $T=0$  for optimally doped samples and quadratic in temperature on the overdoped

side<sup>5</sup>. The Hall angle follows a  $T^2$  dependence<sup>7</sup>. This was interpreted in the framework of Fermi Liquid theory by the existence of hot spots, small regions on the Fermi surface with very short scattering time<sup>8,9,10</sup>, or "cold spots"<sup>11,12</sup>. N. E. Hussey suggested an anisotropic  $T^2$  scattering rate combined with  $T$  independent scattering rate<sup>13</sup>. Other non Fermi liquid ideas involved, two different scattering times for the charge and spin channels,<sup>14</sup> or the Marginal Fermi Liquid theory with a linear in  $T$ , isotropic scattering rate and a temperature independent small angle impurity scattering<sup>15</sup>. In overdoped  $\text{Bi}_2\text{Sr}_{2-x}\text{La}_x\text{CuO}_6$ <sup>16</sup> and in  $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_y$ <sup>17</sup> a deviation from the  $T^2$  behaviour was observed, the exponent  $\alpha$  in the fit  $\cot(\theta_H) = a + bT^\alpha$  decreased with increasing doping. This behaviour was interpreted as a contribution of extended regions on the Fermi surface to the Hall angle as the doping level increases<sup>13</sup>.

In the electron doped cuprates, Woods *et al.*<sup>18</sup> reported that in optimally doped samples  $\alpha$  is twice as large as the resistivity exponent. They interpreted this behavior in the framework of the theory of Abrahams and Varma<sup>15</sup>. A possibility of hole superconductivity in the electron-doped cuprates was speculated by Z. Z. Wang *et al.*<sup>19</sup> on the basis of Hall and resistivity measurements for presumably overdoped samples. W. Jiang *et al.*<sup>1</sup> suggested that holes are crucial for the occurrence of superconductivity in electron-doped superconductors based on magneto-transport measurements on oxygen treated  $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-\delta}$ . Qazilbash *et al.*<sup>20</sup> have shown from Raman spectroscopy measurements that superconductivity in the electron-doped is primarily due to pairing and condensation of hole-like carriers. It was also theoretically predicted that superconductivity will be favored by having hole states rather than electron ones at the Fermi energy<sup>4</sup>.

The detailed doping and temperature study of resistivity and Hall angle reported here enables us to qualitatively follow the contributions of electrons and holes

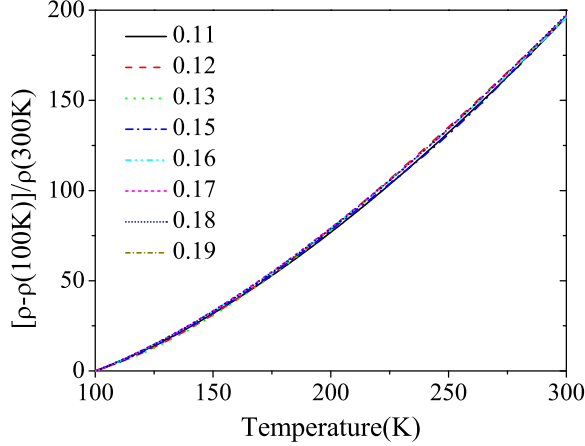


FIG. 1: Normalized resistivity from 100K to 300K. The resistivity at 100K is subtracted from  $\rho(T)$  then all curves are normalized at 300K. Except for a residual term and a coefficient all doping concentrations exhibit the same temperature dependence.

to the transport and to deduce their respective roles in generating the superconducting condensate.

## II. SAMPLES PREPARATION AND MEASUREMENTS.

$\text{Pr}_{2-x}\text{Ce}_x\text{CuO}_4$  *c*-axis oriented films of various cerium doping concentrations:  $x = 0.11, 0.12 \dots 0.19$  were deposited from stoichiometric targets on (100) oriented  $\text{SrTiO}_3$  substrates using the pulsed laser deposition technique as described elsewhere<sup>21</sup>. The films were patterned to form Hall bars using ion milling. The Hall angle was measured at 14T where all the samples are normal and  $\rho_{xy}$  has a linear dependence on magnetic field. The normal state resistivity and the superconducting transition temperatures and widths are identical to the previously reported data<sup>21</sup>

## III. RESULTS AND DISCUSSION.

First, we show, that in a strong contrast to the hole doped cuprates, the doping level has no influence on the temperature dependence of the resistivity,  $\rho$  and that the resistivity is dominated by the electrons. In figure 1 we plot  $[\rho(T) - \rho(100K)]/\rho(300K)$ . This merely cancels the contribution of any residual impurity scattering and divides each curve by a numerical factor. We chose 100 K for two reasons: a) at this temperature all the resistivity curves have approximately the same slope; b) this temperature is still well above the upturn in the resistivity. Remarkably, all the data collapse on a single

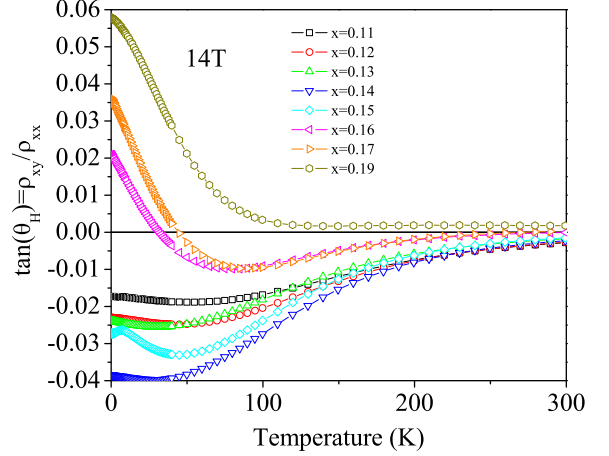


FIG. 2:  $\tan \theta_H = \rho_{xy}/\rho_{xx}$  at 14T as a function of temperature for the various doping levels.  $\tan \theta_H(T)$  has a clear doping dependence.

curve. The non superconducting sample  $x = 0.11$  scales together with all the other superconducting ones. In this sample there are no holes as can be inferred from high field Hall measurements, where  $\rho_{xy}$  is found to be linear in  $H$  and negative up to 60 T at 100K<sup>22</sup> as expected for a single type of carrier. We can therefore conclude that the doping independent behavior of the resistivity for  $x = 0.11 - 0.19$  must be due to the electrons. We note that such data collapse is not possible for the hole-doped cuprates where the temperature dependence of the resistivity changes from linear to quadratic as the doping is increased.

Second, we show that the Hall angle is sensitive to the doping level and that optimum doping can be identified using this property. This result is due to a hole contribution to the transverse resistivity. In Figure 2 we show  $\tan(\theta_H)$  at 14T for  $0.35K < T < 300K$  for  $x = 0.11, 0.12 \dots 0.19$ . The Hall angle changes sign with doping and temperature. This indicates that the transverse resistivity is sensitive to both holes and electrons. The reported  $T^2$  dependence of  $\cot(\theta_H)$  for hole doped cuprates is not seen here. Instead  $\alpha$ , the exponent obtained from the fit to  $\cot(\theta_H) = a + bT^\alpha$  for  $100K < T < 300K$ , changes with doping. In Figure 3,  $\cot(\theta_H)$  is shown for under-to-optimally doped  $\text{Pr}_{2-x}\text{Ce}_x\text{CuO}_4$ ,  $x = 0.11 - 0.15$ , as a function of  $T^\alpha$ . The exponent  $\alpha$  increases monotonically from 3.24 for  $x = 0.11$  to 4 for  $x = 0.15$ . For the overdoped region ( $x \geq 0.16$ ) the power law behavior is lost and such a fit is not possible. The exponent found for  $x = 0.15$  is consistent with previous reports<sup>2,18</sup>. While the resistivity above  $T_c$  can give no indications for the doping level, the doping level and in particular that of maximum  $T_c$  can be identified using the exponent of  $\cot(\theta_H)$  at least on the under-to-optimum doping regime ( $0.11 \geq x \geq 0.15$ ) even

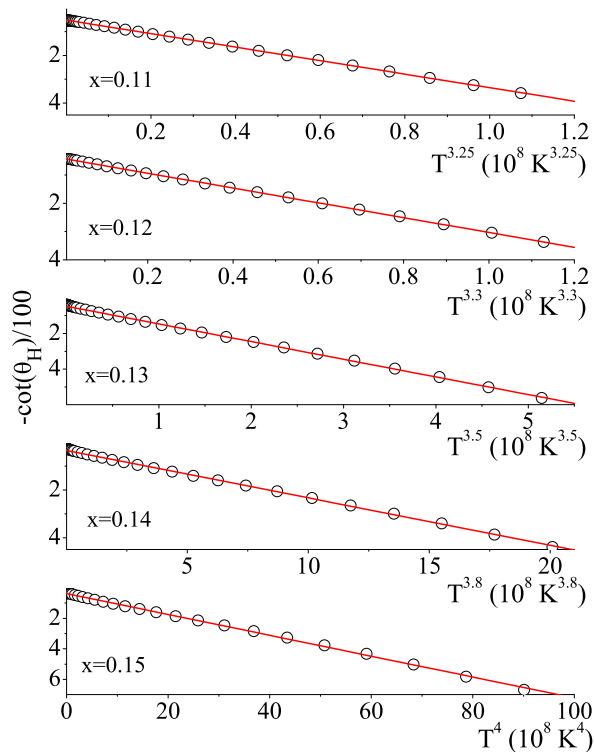


FIG. 3:  $\cot \theta_H$  as a function of  $T^\alpha$ , where  $\alpha$  is found from a fit to  $\cot(\theta_H) = a + bT^\alpha$  for the temperature range 100-300 K. Note that  $\alpha$  increases with increasing doping. For  $x \geq 0.16$   $\cot(\theta_H)$  cannot be fit to a power law.

at relatively high temperatures as can be clearly seen in Figure 3.

In hole doped cuprates  $\alpha$  decreases when the doping is increased from optimum to the overdoped region<sup>16,17</sup>. A similar, but mirror like, picture is seen here for the optimum to underdoped region, where  $\alpha$  increases with increasing doping reaching its maximum value at optimum doping (before the power law behaviour is lost). It was suggested that the difference between the Hall and resistivity temperature dependences in hole doped cuprates is coming from the hot-spots on the Fermi surface<sup>13</sup>. For electron-doped cuprates ARPES measurements have found that the hot-spots can be seen most clearly at optimum doping. Since most of the scattering takes place at these (hole like) hot spots one expects the largest difference between the resistivity and the Hall angle exponents at this doping level, as seen in Figure 3. At low dopings the Fermi surface consists only of electron pockets<sup>3</sup>. In this case electrons should dominate both resistivity and Hall angle. One should therefore expect the exponents of these two transport properties to become closer as the doping level is decreased from optimum, as observed. Summarizing, the behavior of the Hall angle is consistent with both hole and electron regions on the Fermi surface contributing to the transverse resistivity.

Although the Fermi surface is electron like from  $x = 0.11$  all the way up to optimum doping, as inferred from the negative sign of  $R_H$  at all temperatures<sup>21</sup>, there is a strong hole contribution to  $R_H$  in optimally doped samples. This is suggested by the steep rise in  $R_H$  towards positive values as the temperature is decreased below 67 K<sup>19,21</sup>. Above optimum doping the Fermi surface rearranges and becomes hole like, presumably at a quantum critical point<sup>21</sup>. Away from this quantum critical point there is a funnel shaped region of quantum and thermal fluctuations in the doping-temperature phase diagram, resulting in the reappearance of both the electron and the hole bands at higher temperatures even for overdoped samples. The phase diagram presented by Li *et al.*<sup>22</sup> from high field Hall and magnetoresistance measurements may define these different regions. At low temperatures ( $T < 10K$ ) on the overdoped side ( $x \geq 0.17$ ), outside of the funnel shaped region of quantum fluctuations, the resistivity and  $\cot(\theta_H)$  follow the same temperature dependence, thus suggesting a metallic-like single band Fermi surface. Additional evidence for the dominance of a single band at low temperatures is found from thermopower and Hall measurements<sup>21,23</sup>. These two transport properties yield exactly the same carrier concentrations at low temperatures when analyzed using simple single band Drude mode. We also note that for the overdoped side as the Ce concentration is increased the number of holes and  $T_c$  decrease. The reason for the vanishing of  $T_c$  in both types of cuprate is yet to be understood.

The origin of the resistivity behavior at high temperatures is unclear at the moment. Its doping independence suggests that it is unrelated to the antiferromagnetic order or to the hot spots in the Fermi surface. Hublina and Rice<sup>24</sup> showed that cold regions can short out the effect of the hot spots on the Fermi surface. This results in a resistivity which is insensitive to the hot spots (and doping). In our case not only is the resistivity (above 100K) insensitive to the hot spots but also to the development of the hole like regions on the Fermi surface. This dominance of the electrons needs further theoretical investigation. While the electron-doped resistivity is very different from that of the hole-doped cuprates there is some resemblance in the behavior of the Hall resistivity (or the Hall angle) for the two types of cuprates. First, it has a doping dependence even at high temperatures and optimum doping can be identified using the power of the temperature dependence of  $\cot(\theta_H)$ . Second, a strong hole contribution to  $R_H$  appears at optimum doping. This leads us to conclude that holes play a similar role in both types of superconductor. The absence of a hole contribution in the underdoped, non-superconducting, samples and the lack of a doping dependence for the electron-dominated resistivity, strongly suggest that electrons have no (or a very small) contribution to superconductivity in the electron-doped cuprate superconductors.

#### IV. SUMMARY

We measured the resistivity and the Hall angle of  $\text{Pr}_{2-x}\text{Ce}_x\text{CuO}_4$  as a function of temperature and doping from  $x = 0.11$  (underdoped and nonsuperconducting) to  $x = 0.19$  (very overdoped). While the temperature dependence of the resistivity between 100K and 300K show no variation with doping, the exponent  $\alpha$  of the Hall angle in the fit  $\cot(\theta_H) = a + bT^\alpha$  exhibits doping dependence. This quantity can be correlated with the occurrence of superconductivity. We have shown that the resistivity is mostly sensitive to the electrons while the transverse resistivity probes both the hole and elec-

tron regions on the Fermi surface. Our results lead us to conclude that in electron-doped cuprates holes are responsible for superconductivity.

#### Acknowledgments

We thank Guy Deutscher and Girsh Blumberg for very useful discussions. Support from NSF grant number DMR-0352735 is acknowledged for work at the University of Maryland. Y.D. wishes to thank the German Israeli foundation for support.

- 
- \* yodagan@post.tau.ac.il
- <sup>1</sup> W. Jiang, S. N. Mao, X. X. Xi, X. Jiang, J. L. Peng, T. Venkatesan, C. J. Lobb, and R. L. Greene, Phys. Rev. Lett. **73**, 1291 (1994).
  - <sup>2</sup> P. Fournier, X. Jiang, W. Jiang, S. N. Mao, T. Venkatesan, C. J. Lobb, and R. L. Greene, Phys. Rev. B **56**, 14149 (1997).
  - <sup>3</sup> N. P. Armitage, F. Ronning, D. H. Lu, C. Kim, A. Damascelli, K. M. Shen, D. L. Feng, H. Eisaki, Z.-X. Shen, P. K. Mang, et al., Phys. Rev. Lett. **88**, 257001 (2002).
  - <sup>4</sup> J. E. Hirsch, Phys. Rev. B **48**, 3327 (1993), and references therein.
  - <sup>5</sup> H. Takagi, B. Batlogg, H. L. Kao, J. Kwo, R. J. Cava, J. J. Krajewski, and W. F. Peck, Phys. Rev. Lett. **69**, 2975 (1992).
  - <sup>6</sup> H. Matsui, K. Terashima, T. Sato, T. Takahashi, S.-C. Wang, H.-B. Yang, H. Ding, T. Uefuji, and K. Yamada, Physical Review Letters **94**, 047005 (2005).
  - <sup>7</sup> T. R. Chien, Z. Z. Wang, and N. P. Ong, Phys. Rev. Lett. **67**, 2088 (1991).
  - <sup>8</sup> A. Carrington, A. P. Mackenzie, C. T. Lin, and J. R. Cooper, Phys. Rev. Lett. **69**, 2855 (1992).
  - <sup>9</sup> B. P. Stojković and D. Pines, Phys. Rev. Lett. **76**, 811 (1996).
  - <sup>10</sup> H. Kontani, K. Kanki, and K. Ueda, Phys. Rev. B **59**, 14723 (1999).
  - <sup>11</sup> L. B. Ioffe and A. J. Millis, Phys. Rev. B **58**, 11631 (1998).
  - <sup>12</sup> A. T. Zheleznyak, V. M. Yakovenko, and H. D. Drew, Phys. Rev. B **59**, 207 (1999).
  - <sup>13</sup> N. E. Hussey, Eur.Phys.J. B **31**, 495 (2003).
  - <sup>14</sup> P. W. Anderson, Phys. Rev. Lett. **67**, 2092 (1991).
  - <sup>15</sup> E. Abrahams and C. M. Varma, Phys. Rev. B **68**, 094502 (2003).
  - <sup>16</sup> Y. Ando and T. Murayama, Phys. Rev. B **60**, R6991 (1999).
  - <sup>17</sup> Z. Konstantinović, Z. Z. Li, and H. Raffy, Phys. Rev. B **62**, R11989 (2000).
  - <sup>18</sup> S. I. Woods, A. S. Katz, S. I. Applebaum, M. C. de Andrade, M. B. Maple, and R. C. Dynes, Phys. Rev. B **66**, 014538 (2002).
  - <sup>19</sup> Z. Z. Wang, T. R. Chien, N. P. Ong, J. M. Tarascon, and E. Wang, Phys. Rev. B **43**, 3020 (1991).
  - <sup>20</sup> M. M. Qazilbash, A. Koitzsch, B. S. Dennis, A. Gozar, H. Balci, C. A. Kendziora, R. L. Greene, and G. Blumberg, Phys. Rev. B **72**, 214510 (pages 12) (2005).
  - <sup>21</sup> Y. Dagan, M. M. Qazilbash, C. P. Hill, V. N. Kulkarni, and R. L. Greene, Physical Review Letters **92**, 167001 (2004).
  - <sup>22</sup> P. Li, F. F. Balakirev, and R. L. Greene, cond-mat/0702534.
  - <sup>23</sup> P. Li, K. Behnia, and R. L. Greene, Phys. Rev. B **75**, 020506 (2007).
  - <sup>24</sup> R. Hlubina and T. M. Rice, Phys. Rev. B **51**, 9253 (1995).